Review on Shear Thickening Fluids and Applications

Jie Ding[1*], Phillip Tracey [2], Weihua Li[3*], Gangrou Peng [3], Philip G. Whitten[3], Gordon G. Wallace[2]

[1]Land Division, Defence Science & Technology Organisation, VIC 3207, Australia
[2]Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, AIIM Facility, Innovation Campus, University of Wollongong, Wollongong, NSW 2522 Australia
[3]School of Mechanical, Materials & Mechatronic Engineering, Faculty of Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

Jie.Ding@dsto.defence.gov.au; weihuali@uow.edu.au

Abstract

Recently, research in the area of shear thickening fluids (STFs) has increased due to the potential for commercial application. They are considered possible candidate materials for liquid body armour and sporting protective clothing and other applications because of their unique properties. Here the state of the art of shear thickening mechanisms, ingredient materials, fabrication methods, rheological properties, and factors influencing shear thickening behaviour have been reviewed. Basic models used to describe shear thickening behavior are also discussed. Relevant patent applications, particularly in the area of body armour, as well as other industrial applications, such as smart structures, and devices with adaptive stiffness and damping, are also summarized. Recent advances, including the effects of particle surface properties, relationship to carrier fluids and electric or magnetic fields applied on the transition of STFs are included in the review.

Keywords

Shear Thickening Fluids; Rheological Properties; Smart Structure; Viscosity; Body Armour; Nanoparticles

Introduction

Concentrated particle suspensions are found in many formulations such as paint, inks, ceramics and concrete in consumer products including food and cosmetics, and in natural systems such as the flow of blood [Kalman (2010)]. The rheological behavior in such system can vary greatly. Shear thinning, shear thickening, thixotropy, yielding, and shear induced aggregation [Barnes (1989), Wagner (2009)] have been observed. The nonlinear rheological behaviour of particle suspensions arises from a micro-structural rearrangement of the particles within the system. The non-linear rheological behaviour of interest here is shear thickening, an increase in viscosity as an applied shear rate or shear stress increases. It is an example of a non-Newtonian fluid, often termed as a dilatant fluid. At low shear rates, the fluid has low viscosity, acts as a lubricant and flows easily. However, when an impact is applied (at higher shear rates), the fluid adopts a solid-like state and due to a rapid increase in viscosity becomes less penetrable.

Shear thickening has long been a topic of interest, although it was initially only seen as a problem, complicating and limiting the rate of industrial processes which involve the combination of high shear rates and highly concentrated suspensions such as paper coating and the pumping of slurries. More recently, the property has seen used in developing smart materials and composites [Wagner (2009), Cheng *et al.* (2011), Brown *et al.* (2010), Waitukaitis and Jaeger (2012), Brown and Jaeger (2009), Smith *et al.* (2010), Bi at al. (2011), Roché *et al.* (2011)] as their unique material properties make them ideal for many applications [Wagner (2009), Beiersdorfer *et al.* (2011), Liu *et al.* (2010)], including liquid body armour [Li *et al.* (2008)]. Various mechanisms have been proposed for the operation of STFs, including the formation of particle clusters by hydrodynamic lubrication forces [Wagner (2009), Cheng *et al.* (2011)], granular dilation [Cheng *et al*. (2011)], or impact activated solidification [Waitukaitis and Jaeger (2012)]. The actual nature of the shear thickening depends on the physical parameters of the suspended phase: phase volume, particle size (distribution) and particle shape, as well as those of the suspending phase: viscosity and details of deformation (including shear or extensional flow, steady or transient, time and rate of deformation) [Barnes (1989)].

Composition and Fabrication Methods of STFs

Particle Based Shear Thickening Systems

A STF is composed of a carrier liquid and rigid, colloidal particles, with an example commonly seen in

research being colloidal silica particles suspended in polyethylene glycol. The particles are generally selected from a number of the groups which include titanium oxide, calcium carbonate, cornstarch, synthetically and naturally occurring minerals, polymers or a mixture of these. Some of these shear thickening fluids are discussed in the patents [Savins (1968), Savins and Metzner (1968)] issued to Savins and Wagner *et al.* Many carrier fluids have been investigated, including water, ethylene glycol (EG) and polyethylene glycol (PEG). EG or PEG are the most widely used due to their combination of stability, high boiling point, polarity and non-flammable properties [Chen *et al*. (2005)].

STF dispersions typically fall into the colloidal size range with particle size within the range of 1 nm to 1 μm. The preparation of most simple STFs involves the addition of particles to the carrier fluid using a low speed mixer. STF containing composites have been formed by blending the STF within the rubber precursors and then adding the catalyzing agent [Wagner *et al*. (2010)]. The resultant rubber exhibited shear thickening properties. Adding a STF to open cell polyurethane created a Foam-STF composite, and this was found to exhibit a significant shear thickening response [Wagner *et al*. (2010)]. STF composites have also been formed by polymer blending, leading to materials with unique and superior performance, such as foam composites, which became solid like and absorbed energy at high strains while still maintaining a fluid-like response at low strain rates as a consequence of the STF content and multiphase microstructure [Wagner *et al*. (2010)]. A novel STF composite was also reported [Caritey and Melaine (2010)], made by combining an amphiphilic polymer, hydrophilic particles and PEG, such composition showed shear-thickening properties [Ueno *et al*. (2011)].

Non-particle based Shear Thickening Systems

Although not considered in detail here, there are several important non-particle based shear thickening systems including segmental mobility of polymers about their glass transition and physically cross-linked polymer networks.

All amorphous polymer systems exhibit a glass transition temperature which is the consequence of segmental mobility. When any amorphous polymer is in the glass transition, it will shear thicken when the shear rate is increased [Montgomery *et al*. (2005)].

Polymer networks that are cross-linked via physical bonds will shear thicken when the energy of the physical bond is of a similar magnitude to thermal energy. At low shear rates, the physical bonds are considered to be intermittent, with liquid behavior. At high shear rates, the physical bonds are considered to be fixed resulting in solid like behavior. Poly (vinyl alcohol) containing boric acid, and, poly (dimethylsiloxane) containing boric acid (key ingredients in Silly Putty™) are two well known examples.

Rheological Properties of STFs

Shear thickening is commonly observed in concentrated suspensions undergoing high shear rate. In low concentration suspensions, there is little change in the particle microstructure so nonlinear effects are not typically observed. In most cases, shear thickening results from a stable suspension becoming flocculated due to forces experienced under shear, a mechanism discussed in greater detail later. For this to occur, the suspension must begin in a non-flocculated state resulting from no net attractive forces between particles. Particles may be stabilized by electrostatic forces, steric forces, or solvation forces.

In most cases, a suspension will display either Newtonian or shear thinning behaviour, or both, at low shear rates. At higher shear rates, the fluid will transition into a shear thickening regime which typically lasts no more than one order of magnitude of shear rate before transitioning into another shear thinning region [Galindo-Rosales *et al*. (2011)]. The onset of this transition is commonly characterized by the critical shear rate, or critical shear stress, and can vary significantly between systems. Figure.1 shows an example of viscosity versus shear rate for Polymethylmethacrylate (PMMA) dispersed in a glycerine–water mixtures with various different ratios [Jiang *et al*. (2010)]. This viscous increase occurs at a critical shear rate. In addition, the suspension behaves as a Newtonian fluid across a large spectrum of shear rates, except for the transition shear rate period. These types of fluids have been characterized as Newtonian fluids with a low viscosity before the critical shear rate transition, and as quasi-Newtonian fluids, but with a higher viscosity, after the transition [Laun *et al*. (1991)]. There has been some research into the dynamic properties of STFs. Laun *et al.* reported the critical strain amplitude for dynamic shear thickening at a fixed angular frequency of a polymer latex dispersion. Raghavan *et al.* [Raghavan *et al*. (1997)] investigated the shear thickening response of fumed silica

suspensions under steady and oscillatory shear and Fischer *et al.* [Fischer *et al.* (2006)] investigated the dynamic properties of STF based on a vibrating sandwiched beam.

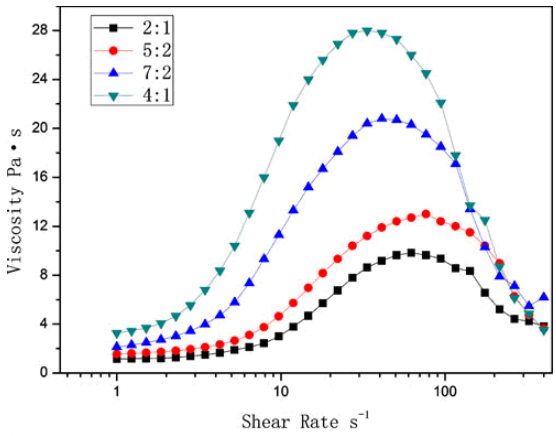

FIG.1 VISCOSITY VERSUS SHEAR RATE FOR PMMA VOLUME FRACTION 52% DISPERSED IN GLYCERINE–WATER MIXTURES WITH DIFFERENT RATIOS: 2:1, 5:2, 7:2, AND 4:1. STEADY SHEAR SWEEPS AT $\dot{\Gamma}$ = 1–400 S^{-1}[Jiang *et al*. 2010].

The degree to which the viscosity increases over this shear thickening region can also vary greatly between systems, from the modest increase to an increase of several orders of magnitude. In some cases discontinuous shear thickening is seen, characterised by a sharp jump in stress with increasing shear rate. This is effectively a liquid to solid transition and the material may even crack like a solid [Brown et al. (2012)]. This process is completely reversible, and the material will return to a viscous liquid again after the stress is removed. The shear rate at which these transition occur and the magnitude of the viscosity increase are determined by a number of factors, including particle concentration, size, shape, size distribution and inter-particle interactions.

Factors Affecting Shear Thickening

One of the factors that has shown the largest influence over nonlinear rheological behaviour in suspensions is the volume fraction (ø) of the discrete phase.[Kalman (2010), Barnes (1989), Hoffman (1972), Jones et al. (1991), Boersma *et al*. (1990), Ueno *et al*. (2009), Genovese (2012)] Under dilute conditions (ø ≤ 0:03), interactions between particles are insignificant as the flow field around a particle will not be influenced by other particles. As the particle concentration increases however, there is an increasing likelihood that particles will begin to influence the flow field of other particles, and the particles are said to experience hydrodynamic interactions. At high volume fractions (ø ≥0:30 for spherical particles) these hydrodynamic interactions have a large effect on the flow properties of the suspension [Mewis and Wagner (2012)]. At these high concentrations the viscosity of the fluid becomes sensitive to the shear rate, or equivalently the applied shear stress, as particles are disturbed from their equilibrium spacing.

Figure 2 illustrates the effect of an increasing volume fraction on the shear rate dependence of viscosity for suspensions of 1.25 um polyvinyl chloride spheres dispersed in dioctyl phthalate. At ø= 0:47 a continuous shear thickening region is seen at higher shear rates with a maximum viscosity of 3 Pa.s at 400 s^{-1}. As the volume fraction of particles is increased, this shear thickening region progressively shifts to lower shear rates and the increase in viscosity becomes more dramatic. Above ø = 0:49 the viscosity sharply jumps up, indicating discontinuous shear thickening. These trends have been observed to be consistent in a range of systems and a high concentration of particles is seen as a requirement for the observation of shear thickening at achievable shear rates.

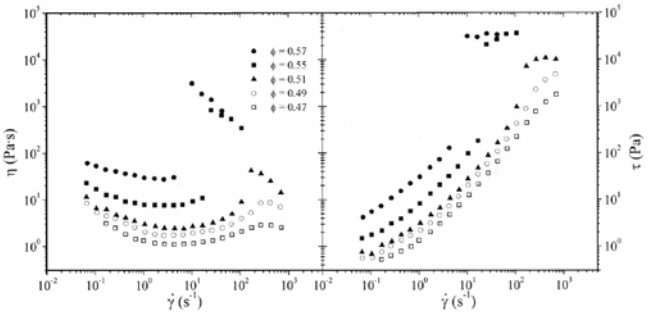

FIG. 2 EFFECT OF VOLUME FRACTION OF 1.25 UM PVC SPHERES IN DIOCTYL PHTHALATE ON VISCOSITY, REPRODUCED FROM HOFFMAN (1972) [Kalman (2010)].

The size of the particles within a suspension also has an effect on its rheological properties [Barnes (1989), Genovese *et al*. (2012),Maranzano and Wagner (2001), Maranzano and Wagner (2001)]. Taking values from many sources in his shear thickening review, Barnes used regression to show the relationship between particle size and critical shear rate, seen in Figure 3a [Barnes (1989)]. No consideration was given in this case to other particle or phase parameters, but there is still a clear trend towards a decreasing critical shear rate as particle size is increased. Providing a more systematic study, Maranzano and Wagner performed studies on a series of chemically similar, monodisperse silica spheres dispersed in an index matched solvent to minimise any other factors, allowing for an accurate study of the effect of particle size on shear thickening [Maranzano and Wagner (2001)]. Figure 3b shows the value of the critical shear rate they obtained for a

number of suspensions with different size particles at different weight fractions, demonstrating the particle size dependence of critical shear rate.

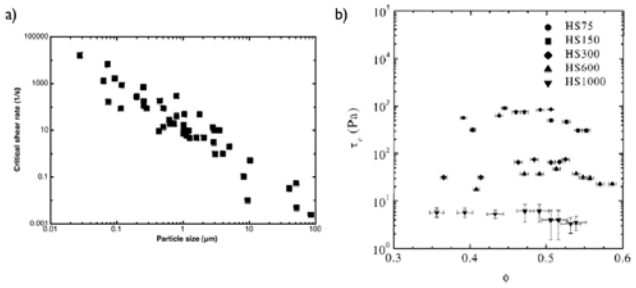

FIG. 3 A) THE CHANGE IN CRITICAL SHEAR RATE AS A FUNCTION OF PARTICLE SIZE, COMPILED FROM A NUMBER OF SOURCES, ADAPTED FROM BARNES (1989)[BARNES (1989)]. B) CRITICAL SHEAR STRESS FOR PARTICLES OF A RANGE OF SIZES AT DIFFERENT WEIGHT FRACTIONS, REPRODUCED FROM MARANZANO (2001)[Maranzano and Wagner (2001)]. THE NUMBER IN THE KEY INDICATES PARTICLE DIAMETER IN NANOMETERS E.G. HS75 = 75 NM DIAMETER PARTICLES.

The discussion concerning particle size was primarily focused on monodisperse suspensions, however, the particle size distribution can have a significant effect. Interestingly, it has been shown that adding small particles of clay to a dispersion of larger particles can actually increase critical shear and reduce the magnitude of shear thickening, despite increasing the total volume fraction of particles. In the same study as the particle size work discussed above, Maranzano and Wagner also studied the effect of mixing particle sizes. Figure 4 shows the steady state viscosity curves for a series of bimodal mixtures of 75 nm particles (HS75) and 1000 nm particles (HS1000) at a constant volume fraction of 0.53. It can be seen that all bimodal mixtures have lower viscosity than the pure particle suspension curves, with a higher critical shear. There is a trend of increasing viscosity as the fraction of smaller particles is increased, despite the pure suspension of larger particles having a significantly lower critical shear than any other mixture [Maranzano and Wagner (2001)].

Particle shape has long been known to have a significant impact on shear thickening, and the effect has been reported a number of times, although the mechanism of action is not completely understood. [Barnes (1989)] In general, anisotropic particles will demonstrate shear thickening at a volume fraction lower than spherical particles. In the case of rod like particles, it has been demonstrated that an increase in aspect ratio corresponds to a decrease in the particle volume fraction required for discontinuous shear thickening. This was initially thought to be due to elongated particles becoming misaligned during the shear thickening transition, however, experiments combining rheological measurements with small angle neutron scattering (SANS) provide evidence that particle alignment is maintained even during this transition [Egres *et al*. (2006)].

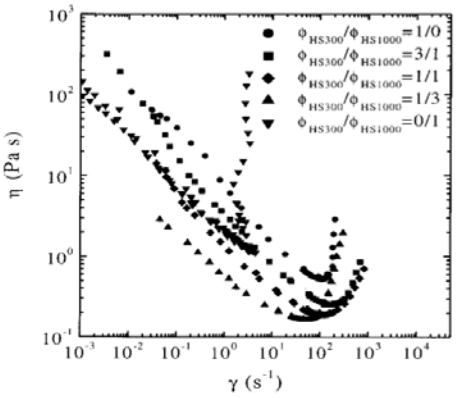

FIG. 4 STEADY SHEAR VISCOSITY AS A FUNCTION OF SHEAR RATE FOR A NUMBER OF BIMODAL PARTICLE SUSPENSIONS, REPRODUCED FROM MARANZANO (2001)[Maranzano and Wagner (2001)].

Fumed silica provides an example of how particle shape can have a remarkable effect with discontinuous shear thickening seen at volume fraction as low as ø = 0.10, see Figure 4, in contrast to the ø ≥0:30 required to observe shear thickening with spherical particles such as those used to obtain the data in Figure 2. This is thought to be due, in part, to the fractal three dimensional aggregates formed by these particles (Figure 5 left). Fumed silica aggregates have a low density and contain continuous pores that are filled by liquid. Hence, the liquid filled aggregates behave as single entities, increasing the effective volume fraction of the particles (Figure 5 right). Fumed silica is also cheap to produce and useful in a number of applications, for this reason, much work has been done to study the rheological behaviour of fumed silica suspensions [Raghavan *et al*. (1997), Brown *et al*. (2011)].

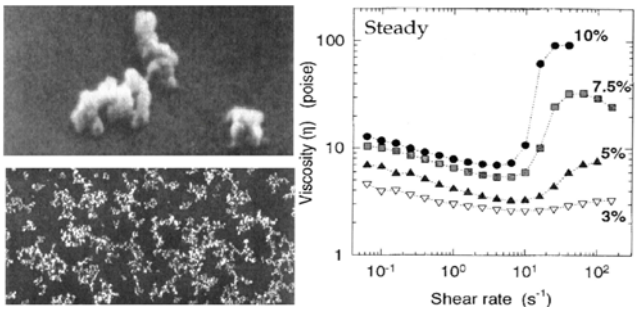

FIG. 5 LEFT: SEM IMAGES OF FUMED SILICA PARTICLES. RIGHT: STEADY SHEAR VISCOSITY AS A FUNCTION OF SHEAR RATE FOR A NUMBER OF DIFFERENT WEIGHT FRACTIONS OF FUMED SILICA IN POLYPROPYLENE GLYCOL, REPRODUCED FROM RAGHAVAN (1997) [Raghavan *et al*. (1997)].

As previously mentioned, for a suspension to be shear thickening, the particles must not readily flocculate, and there must be no net attraction between particles. For this reason, particle-particle interactions are very important. Particles must be stabilized in some way, and this can be achieved in a number of ways. One way is to produce a net repulsion between particles, which can be done by surface modifying them to provide either an electrostatic charge or some kind of steric repulsion. In the common case of silica, an electrostatic charge will naturally form in any solvent which allows for dissociation of surface silanol groups, such as water and ethylene glycol. It has been shown that replacing these surface silanol groups with methyl groups to produce a hydrophobic particle results in the dispersion gelling at low volume fraction and no shear thickening being observed [Laskowski *et al*. (1969)]. If these surface silanol groups are replaced with longer polymer chains however, stable suspensions may be achieved due to steric stabilisation provided by the polymer chains. In cases where surface modification or electrostatic stablisation may not be possible, particles may be suspended in a density matched solvent. Provided the particles behave as hard spheres and there are no attractive forces, the particles will remain stabilised by Brownian motion [Maranzano and Wagner (2001), Melrose *et al*. (2004)].

The effects of electrorheological (ER) or magnetorheological (MR) on shear thickening have been extensively investigated. ER and MR fluids are well known as kinds of smart materials because their structural and rheological changes caused by an electric [Wen *et al*. (2003)] or magnetic field [Guerrero-Sanchez *et al*. (2007)] respectively are typically reversible. Commonly, ER fluids are composed of dispersions of electrically polarizable particles in an insulating fluid. ER fluids exhibit a tremendous increase in their shear viscosity, from a liquid-like to a solid-like state, when they are exposed to a relatively high electric field. This is caused by the formation of chain-like structures of the dispersed particles aligned along the electric field [Choi and John (2009)], which occurs within a few milliseconds of application of the field [Kim *et al.* (2008)]. Typical MR fluids are formulated by dispersion of magnetic particles in an inert (non-magnetic) carrier liquid. These materials show a dramatic but reversible increase in shear viscosity in the presence of an external magnetic field. The change in shear yield stress is due to the magnetic polarization induced in particles, resulting in dipole-dipole interaction forces between particles, which, in turn, leads to the formation of particle chains along the direction of magnetic field.

ER fluids have been applied in various areas such as shock absorbers; engine mounts, and clutches [Han *et al*.(2003)], while MR fluids show potential for applications in the design of dampers, brakes, polishing machines or torque transducers [Goncalves and Carlson (2007)]. Recent research on the combination of ER or MR effects with shear thickening [Brown *et al.* (2010)] has opened up possibilities for the design of field-responsive shear-thickening fluids [Shenoy *at al.* (2003), Zhang *et al.* (2008), Jolly and Bender (2006)]. The applied fields would control the critical shear rate [Zhang *et al*. (2008)], but only for weaker shear-thickening, where both the critical stress and shear rate vary with field. This critical shear rate is controlled by the particle packing fraction [Brown and Jaeger (2009)], whereas the critical stress can be tuned either passively with particle-fluid chemistry or actively with variation of the electric or magnetic field [Brown *et al.* (2010)].

Shear Thickening Mechanism

Whilst shear thickening has been observed and reported for around a century, most early accounts were simply qualitative and did not consider the microstructural rearrangements responsible. The first attempt at explaining the microstructure came from the work by Hoffman in which coupled Rheometry and light scattering techniques was built on packing arguments [Hoffman (1972), Hoffman (1974), Hoffman (1982)]. It was demonstrated by Hoffman that for a number of polymer particle suspensions a diffraction pattern indicative of ordered, hexagonally packed layers appeared prior to the shear thickening transition. Hoffman proposed that these ordered layers formed and moved across each other at low shear rates, resulting in the shear thinning region. At higher shear rates, the repulsive forces between particles are overcome, increasing viscosity. However, with other dispersions, the formation of an ordered structure is prior to shear thickening [Bender and Wagner (1995)].

Simulations and experimentation have since shown that reversible shear thickening results from the formation of hydroclusters, temporary stress bearing aggregates of particles that form as a result of short range hydrodynamic lubrication forces overcoming the repulsive forces between particles during shear, as

shown in Figure.6. Chains of these hydroclusters form as their numbers grow as a result of increased shear rate, resulting in larger aggregates forming which can jam flow [Egres *et al*. (2006)]. An underlying order-disorder transition is not a requirement, but it can occur in some systems prior to hydrocluster formation. A better understanding of this mechanism has allowed for development of a model to predict the critical stress at which shear thickening occurs based on the particle size and interaction potential between particles, which has been verified through experimentation [Maranzano and Wagner (2001)].

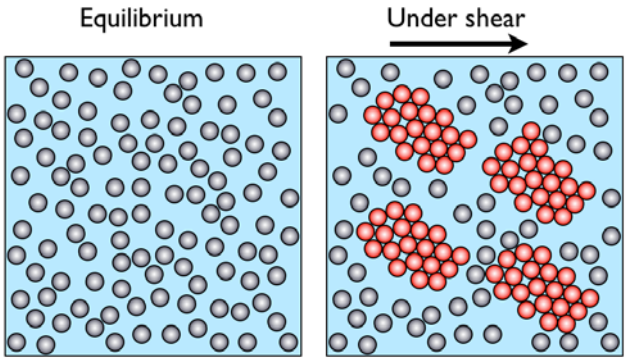

FIG. 6 SCHEMATIC OF PARTICLES FORMING HYDROCLUSTERS UNDER SHEAR.

While this hydrocluster mechanism has become widely accepted for continuous shear thickening, and can provide tools to predict the onset of shear thickening, it is unable to explain the orders of magnitude increase in viscosity during discontinuous shear thickening [Brown *et al*. (2010)]. Recent work by Brown which is built upon packing arguments [Brown and Jaeger (2012)] has proposed that these large increases in viscosity are a result of dilation of the particle packing during onset of shear thickening. This dilation requires that the applied shear stress overcome any interparticle stresses preventing compressive shear between particles and in turn causing the particles to push against the boundary, typically the liquid-air interface when the suspension is open to the air, which pushes back with a restoring force to produce a confining stress on the suspension. The resulting normal forces are transmitted through the fluid by frictional interactions between particles resulting in the rapid increase in shear stress with shear rate characterising discontinuous shear thickening. Brown has further shown that when the fluid is confined, such that there is no liquid-air interface, and that the confining stress is controlled by the stiffness of the most compliant boundary.

Another interesting property of these concentrated suspensions, which has been linked to this model of shear thickening, is the large, positive normal stresses observed under impact. A well-known example is the ability of a person to run across the surface of a concentrated suspension of cornstarch in water. Typically a liquid would flow around an intruding object, however, these suspensions become solid-like under heavy impact. The large forces experienced cannot be sufficiently explained by the hydrocluster model or dilation. Waitukaitis *et al.* have recently performed studies on this phenomenon, exploring the microstructure of a suspension using x-ray scattering and high speed cameras. They have found that the mechanism is more akin to crossing a jamming transition under compression that forms a rapidly growing solid mass which drives flow in the surrounding suspension. This solid mass is transient; however, it has been shown to exhibit a yield stress and elastic properties before melting.

Applications

STFs hold the promise of many industrial applications. Patenting activity has involved both specific applications and the preparation of the STFs themselves. For example, a shear thickening fluid used in conjunction with fabrics was proposed for utilization in an expandable spacecraft [Cohen (2008)]. The combination of the fluid and the fabric was designed to resist penetration by hypervelocity particles in space. Several potential applications for such STFs are covered by patents incorporated into pads for sport equipment, such as a mouthguard for improved energy dissipation. This would hopefully reduce the likelihood of concussion or dental damage. Other applications proposed were gloves, to reduce vibration or protect the hands from jarring impact, or sports shoe designs for energy dissipative construction. Composites composed of discrete droplets or co-continuous networks of STF could also be used in seat cushioning and neck supports in automobiles, aeroplanes and trains to provide increased protection during accidents. Smart materials could be fabricated where the stiffness or hardness of a flexible component can change as a result of deformation, such as from elongation, bending, torque, twisting, or compression. The materials could be used as a medium to control mechanical actuation of one object relative to another[Wagner *et al.* (2006)].

The three main application streams, specifically devices with adaptive stiffness and damping, smart structures and body armour, will be reviewed in more details below.

Devices with Adaptive Stiffness and Damping

The basic idea here is to use STF as a viscoelastic damper to obtain adaptive stiffness and damping [Jolly and Bender (2006)]. When subjected to a predetermined shear rate, the shear thickening composition would undergo a dramatic and substantial increase in viscosity and shear stress. A viscoelastic damper, filled with a STF, could control the vibration of a structural member, or a tank, or a pipe, which might be caused by an earthquake or wind, while providing minimum reaction forces when the component is slowly displaced as a result of the thermal deformation of the member itself or another member connected thereto [Seshimo (1988)].

Smart Structures

Smart structures based on STFs and STF devices used for industrial applications were also investigated. A method to minimize damage to the downhole equipment was described, where the STF was used as a tamp in controlled pulse fracturing (CPF) [Hunt et al. (1991)]. The STF would become more viscous and more resistant to flow up the production string or tubing as fluid velocities increased under the force generated by the ignited propellant. This would slow or even stop the upward movement of structures and the damage to equipment would be lessened [Hunt et al. (1991)]. Another invention presented a method to process composite structures with tailored stiffness and damping performance incorporating a STF, preferably at the interface between two elements belonging to the same structure and moving relative to each other [Hunt et al. (1991)]. The composite structure incorporating STFs, according to the authors, may advantageously be used in applications such as sports equipment, aeronautics, aerospace, consumer goods or in any other suitable field where the dynamic properties of the said structure need to be tailored.

Fisher *et al.* [Fisher *et al.* (2009)] and Helber *et al.* [Helber *et al.* (1990)] investigated the application of STFs in mounting systems for industrial machinery. STFs and STF devices have been developed for application in medical equipment to limit movement of a person's joint such as shoulder, knee, elbow, ankle, hip, etc., so as to prevent the patient from subjecting the joint to sudden rapid acceleration [Williams (2009)]. Such devices can help to limit the attendant damage that could result from such rapid acceleration. A STF was also used for surgical and medical garments to inhibit penetration of garments. Joanna *et al.* [Joanna *et al. (2007)*] reported that the puncture resistance was increased when the STF was incorporated into surgical garments such as surgical gowns, surgical gloves, surgical masks and other wound-care products and the like, where the STF was used as a layer on at least one of the inner and outer surface of the garment. A multi-layered STF composite was prepared for stopping projectiles by Joanna *et al.* [Wasserman *et al*. (2010)]. The composite included a stack comprised of mesh and STF layers. Wasserman *et al.* reported recently [Allen (2008)] that shear thickening compositions can function in an energy or communications transmission cable to provide enhanced protection against externally applied forces, e.g., cutting or puncture from a shovel. The invention was a cable comprising a conductor surrounded by a STF system encased in a cable jacket. The shear thickening composition not only provided protection against mechanical damage but also enhanced the char formation mechanism for superior flame retardance that far surpasses conventional technologies.

Body Armour

Up to now, one of the most important applications of STFs was expected to be protective clothing (also called liquid body armour). Throughout history, personal armour systems have been practical only when they have been able to provide adequate protection against the prevailing threats whilst not impairing the wearer's ability to perform the tasks required. The materials used for current body armour applications are unable to provide the whole body protection due to their stiffness and bulk. Novel liquid body armour based on STFs has shown promising prospects towards improved protection and flexibility. Longer-term research has been performed by the University of Delaware and the US Army Research Laboratory, to use STF fabrics for ballistic, puncture, and blast protection for the military, police, and first responders.

Most liquid body armours, described in recent patents, were formed by immersing a fibrous substrate or a porous media in a STF. Earlier patents used dry powders which exhibited a dilatant property which theoretically increase volume and viscosity under ballistic impact. Dischler *et al* [Dischler *et al.* (1998)] found that KEVLAR fibres coated with a dry powder that exhibits dilatant properties. In this work, the fibres demonstrated an improved ability to distribute energy during ballistic impact due to enhanced inter-fibre friction. Additionally, one or more low glass transition, viscous polymer fluids, as a liquid adhesive

additive, had been impregnated into a fiber structure, such as a polyaramid fabric. A desirable maximum in ballistic penetration resistance and minimum in back face deformation ("BFD", a measure of blunt trauma measured in depth in millimeters where low depth indicates low levels of blunt trauma) was found at a level of content of ~15 wt% or less of the liquid adhesive additive level in the fiber structure. This resulted in a reduction in BFD, while retaining or slightly improving ballistic resistance to penetration [Sauer *et al*. (2005)]. Another patent indicated that the viscous polymers were effective in many different types of fibrous structures with the result of an optimized ballistic resistance as well as protection against blunt trauma in body armour [Sauer *et al.* (2009)]. Poly(dimethylsiloxane), such as Dow Corning 3179 material, a dilatant compound (or a lightweight version) when incorporating Duolite spheres (or a derivative) were incorporated [Plant (2010)]. The dilatant material remained soft and flexible until it was subjected to impact, whereupon its characteristics changed rendering that it was temporarily rigid. The carrier could be coated or impregnated with the dilatant compound in various ways. Using of dry dilatant agents in a fabric carrier to improve ballistic protection was described [Schuster *et al.* (1998)]. In their approach, the dilatant agent was a polymeric powder that was applied to the fabric while suspended in a carrier fluid, and subsequently dried to leave behind the dilatant solid.

The emergence of the STFs as novel protection materials has resulted in more and more patents being filed for liquid body armours or sport and protective clothing. There are many similar patents relating to "liquid body armour", which mostly describe a similar process: diluting the STF in ethanol; saturating Kevlar with the diluted fluid and then placed in an oven to evaporate the free ethanol; the STF then permeating the Kevlar, and the Kevlar strands holding the particle-filled fluid in place. When an object strikes or stabs the Kevlar, the fluid immediately hardens, making the Kevlar ballistically more efficient. The hardening process happens in milliseconds, and the armour becomes flexible again shortly afterward. Decker *et al.* [Decker *et al.* (2007)] investigated the ballistic properties of woven aramid fabrics impregnated with a colloidal, discontinuous STF. An armour composite material which contained a ballistic fabric impregnated with STF was investigated. Such a material seemed to offer superior ballistic performance compared to conventional ballistic fabric-based materials of equal thickness [Wagner and Wetzel (2007), Wagner and Wetzel (2009)]. Lee *et al* [Lee *et al.* (2003)] reported upon the ballistic penetration performance of a composite material composed of woven Kevlar fabric impregnated with a colloidal STF (silica particles (450 nm) dispersed in ethylene glycol). The impregnated Kevlar fabric yielded a flexible, yet penetration resistant composite material. Fragment simulation projectile (FSP) ballistic penetration measurements at ~244 m/s demonstrated the efficacy of the novel composite material. The results demonstrated what was believed to be a significant enhancement in ballistic penetration resistance due to the addition of STF to the fabric, and without any loss in material flexibility. Furthermore, under these ballistic test conditions, the impregnated fabric targets performed equivalently to neat fabric targets of equal area density, while offering significantly less thickness and more material flexibility. The enhancement in ballistic performance was believed to be associated with the shear thickening response, and possible mechanisms of fabric-fluid interaction during ballistic impact were identified. A Kevlar/fabric target impacted at low velocity was discussed by Rosen *et al* [Rosen *et al*. (2007)]. Figure.7. shows targets after ballistic impact. At speeds around or below 144 m/s (Figure. 7a), the K-STF intercalated Kevlar defeated the projectile and only minimal damage was observed. However, at this speed, the projectile would have penetrated neat Kevlar. At higher velocities 144 m/s (Figure. 7b) the projectile was still stopped, but the yarns have undergone large relative displacements without significant fracture. Finally, at velocities above 150 m/s (Figure. 7c), significant fiber fracture occurred and the projectile penetrated. V_{50} is an important criterion in measuring ballistic performance for body armor, at which 50 percent of the shots go through and 50 percent are stopped by the armour. Decker *et al* [Decker *et al.* (2005)] reported V_{50} performance of STF-Kevlar composites. A range of impact velocities was used in order to characterize V_{50} performance of STF Kevlar composites, and the ballistic results clearly show that STF addition substantially improves the V_{50} performance of Kevlar fabric, under their particular ballistic conditions and target configuration, the STF-Kevlar target showed a remarkably higher V_{50} of 248 m/s.

The stab resistance of STF treated Kevlar and Nylon fabrics was investigated [Decker *et al.* (2007)] and found to exhibit significant improvements over neat fabric targets of equivalent area density. Specifically,

dramatic improvements in puncture resistance (spike threat) were observed under high and low speed loading conditions, while slight increases in cut protection (knife threat) was also observed. Studies on the effect of fabric architecture indicate that STF addition provides benefits analogous to the effect of increasing fabric yarn count, with STF addition primarily reducing the mobility of filaments and yarns in the impact zone. Microscopy shows significant energy dissipation in the damage zone that includes plastic flow of the polymeric filaments, as well as deformation of the filaments due to mechanical interaction with the colloidal particles of the STF. These results indicate that these novel materials could be used to fabricate flexible body armours that provide improved protection against stab threats. Figure.8. and Figure.9. show the drop tower stab performance of the Kevlar and STF–Kevlar targets against the spike impact. The STF–Kevlar target shows significantly better stab resistance compared with the Kevlar target that exhibits the maximum measurable penetration, five witness layers, at energy of only 4 J. In contrast, even at the highest energy level of 17 J, the STF–Kevlar targets only allow penetration through three witness layers. Furthermore, STFs were enhanced and integrated into a flowable and deformable composite structure, which included reinforcement by "stiff" materials, i.e., materials with high compression strength and high bending modulus, such as, but not limited to, short inert fibres less than 1 cm in length [Wagner and Wetzel (2009)].

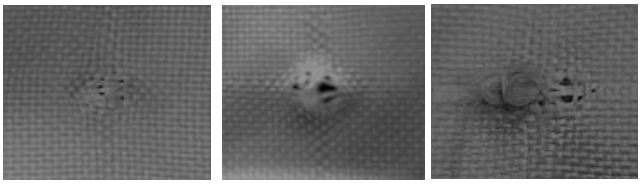

FIG. 7 K-STF COMPOSITE SAMPLES AFTER BALLISTIC TESTING. (a) PARTIAL PENETRATION AT144M/S, (b) PARTIAL PENETRATION AT 147M/S, (c) COMPLETE PENETRATION AT 150M/S [Decker *et al.* (2005)].

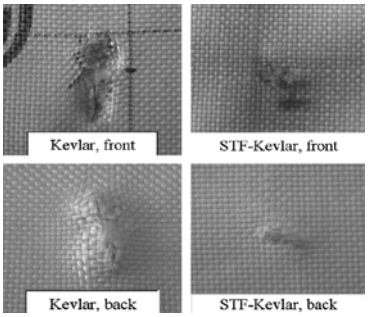

FIG. 8 PHOTOGRAPHS OF KEVLAR AND STF–KEVLAR FABRIC DAMAGE AT M = 2.34 KG AND H = 0.75 M OF KNIFE DROP.

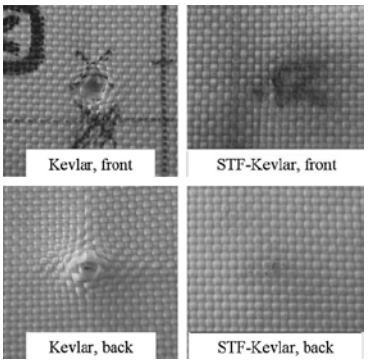

FIG. 9 PHOTOGRAPHS OF KEVLAR AND STF–KEVLAR FABRIC DAMAGE AT M = 2.34 KG AND H = 0.75 M OF SPIKE DROP [68].

For such novel liquid body armour based on STFs, promising results have been shown towards improved protection and flexibility. However, "liquid body armour" applications still suffer several drawbacks, including evaporation, sensitivity to humidity, and leakage of carrier fluids and reduced air and/or moisture permeability which affects the comfort of clothing. Most liquid body armours have been formed by immersing a fibrous substrate or a porous media in a STF. However, impregnated fibres or porous media have the disadvantage in that when the STF is exposed to the elements, the performance of the fabric suffers because of evaporation and leakage of the STF. Therefore, the evaporation of the carrier fluid is a key issue in the current STF research. For example, typical STF composed of silica nanoparticles suspended in an EG fluid is likely to suffer evaporation of the EG into the air even though its boiling point is as high as 197°C. Considerable efforts have been made in recent years to solve this problem, including filling a hollow fibre with a STF [Borella *et al*. (2008)]. However, a STF, by its nature, is not easily pumped into hollow fibres. In order to pump the STF into the fibres, the viscosity of the STF has to be decreased, but in this case the shear response of STF will be affected accordingly.

Another critical requirement for soft and comfortable body armour, apart from strong protection, is reasonably high permeability to air and moisture, so that it is comfortable to wear. Research on STF-based liquid body armour is an ongoing activity at the U.S. Army Research Laboratory, the University of Delaware [Wagner (2009)], and the Massachusetts Institute of Technology (MIT) [Deshmukh and Mckinley (2007)].

A novel engineered material dee-three-oh (d3o) which employs shear thickening fluid based on a special gel has been developed by the UK company d3o. Such soft gel is able to flow with moving but on shock it locks together to absorb the impact energy.

Conclusions

This paper presents a review of the state of the art in STF technology. There is a growing need to understand all aspects of STFs, to model their behaviors and to improve applications by optimizing components and fabrication procedures. This review shows that there is significant research in progress that is continually developing new STFs with new carrier fluids and/or particles, optimized conditions or novel manufacturing techniques to meet new and more demanding requirements.

The development of new STFs based on novel nanoparticles that have tuneable properties has attracted more and more attention for both its scientific challenges and its wide potential applications. Recent research has indicated that shear thickening can be controlled by changing the surface properties of particles (e.g. hydrophilic or hydrophobic), roughness, shapes and measuring conditions. The findings open up possibilities for new designs of smart suspensions that could combine shear thickening with control of particle surface properties, electro- or magnetorheologic response, thus producing specific STFs for different applications, and certainly widening the potential applications of STFs.

ACKNOWLEDGMENT

This research was supported by DSTO Fellowship Program from Defence Science and Technology Organisation, Australian.

REFERENCES

Allen, S.D., 2008. Body limb movement limiter. US7402147.

Barnes, H. A., 1989. Shear-thickening ("dilatancy") in suspensions of non-aggregating solid particles dispersed in newtonian liquids. Journal of Rheology 33(2), 329-366.

Beiersdorfer, P., Layne, D., Magee, E. W., Katz, J. I., 2011. Viscoelastic suppression of gravity-driven counterflow instability. Phys. Rev. Lett. 106, 058301.

Bender, J. W., Wagner, N. J., 1995. Optical Measurement of the Contributions of Colloidal Forces to the Rheology of Concentrated Suspensions. Journal of Colloid and Interface Science 172(1), 171-184.

Bi D., Zhang J., Chakraborty B., Behringer R. P., 2011. Jamming by shear. Nature 480, 355-358.

Boersma, W.H., Laven, J., Stein, H.N., 1990. Shear thickening (dilatancy) in concentrated dispersions. AIChE Journal 36(3), 321-332.

Borella R.B., Barry R.P., Allgeuer T.T., 2008. Den Hartog H. Plastic hollow fibre containing a shear thickening fluid for high tensile strength fibres. US2007000901258.

Brown, E. *et al*., 2010. Generality of shear thickening in dense suspensions. Nature Mater. 9, 220–224.

Brown, E., Jaeger, H. M., 2012. The role of dilation and confining stresses in shear thickening of dense suspensions. Journal of Rheology 56 (4), 875-923.

Brown, E., Jaeger, H., 2009. Dynamic jamming point for shear thickening suspensions, Phys. Rev. Lett. 103, 086001.

Brown, E., Zhang, H., Forman, N. A., Maynor, B.W., Betts, D. E., DeSimone, J. M., Jaeger, H. M., 2011. Shear thickening and jamming in densely packed suspensions of different particle shapes. Physical Review E 84(3), 031408-031419

Caritey, Jean-philippe, C., Melanie. C., 2010. Polymers and nanoparticles formulations with shear-thickening and shear-gelling properties for Oilfield applications. US20100071893A1.

Cheng X., McCoy, J. H., Israelachvili, J. N., Cohen, I., 2011. Imaging the microscopic structure of shear thinning and thickening colloidal suspensions. Science 333, 1276–1279.

Chen, J, Spear, S. K., Huddleston, J. G., Rogers, R. D. 2005. Polyethylene glycol and solutions of polyethylene glycol as green reaction. Green Chemistry 7(2), 64-82.

Choi H. J., John M.S., 2009. Electrorheology of polymers and nanocomposites. Soft Matter 5,1562-1567.

Cohen, D. 2008. Shear-thickening fluid reinforced fabrics for use with an expendable spacecraft. US0296435.

Decker M. J., Egres R. J., Wetzel, E. D., Wagner N. J., 2005. Low Velocity Ballistic Properties of Shear Thickening Fluid (STF)– Fabric Composites, To appear in Proceedings of 22nd International Symposium on Ballistics. Vancouver, BC. November 14-18.

Decker M. J., Halbach C. J., Nam C. H., Wagner N. J., Wetze E. D., 2007. Stab resistance of shear thickening fluid (STF)- treated fabrics. Compos. Sci. Techn. 67, 565-578.

Deshmukh S. S., McKinley G. H., 2007. Adaptive energy-absorbing materials using field-responsive fluid-impregnated cellular solids. Smart Mater. Struct. 16, 106-13.

Dischler, L. M., Terry, T., Henson, J. B., 1998. Dilatant

powder coated fabric and containment articles formed therefrom. US5776839.

Egres, R. G., Nettesheim, F., Wagner, N. J., 2006. Rheo-SANS investigation of acicular-precipitated calcium carbonate colloidal suspensions through the shear thickening transition. Journal of Rheology 50(5), 685-709.

Fischer, C., Braun, S.A., Bourban, P. E., Michaud, V., Plummer, C. J. G., Manson, J. A. E., 2006 Dynamic properties of sandwich structures with integrated shear-thickening fluids. Smart Mater Struct, 15, 1467-75.

Fischer, C., Neagu, R. C., Bourban, P.E., Michaud V., Plummer C. J. G., Lavanchy S., Manson J. A. E., 2009. Structures with adaptive stiffness and damping integrating shear thickening fluids. WO2009053946.

Galindo-Rosales, F. J., Rubio-Hernandez, F. J., Sevilla, A., 2011.An Apparent Viscosity Function for Shear Thickening Fluid. Journal of Non—Newtonian Fluid Mech 166, 321-325

Genovese, D. B., 2012. Shear rheology of hard-sphere, dispersed, and aggregated suspensions, and filler-matrix composites. Advances in Colloid and Interface Science 171, 1-16.

Goncalves F. D., Carlson J. D., 2007. Investigating the time dependence of the MR effect. Int. J. Mod. Phys. B 21, 4832-4840.

Guerrero-Sanchez C, Lara-Ceniceros T, Jimenez-Regalado E, Rasa M Schubert US, 2007. Magnetorheological fluids based on ionic liquids. Adv Mater 19, 1740-1747.

Han Y.M., Lim S.C., Lee H.G., Choi S.B., Choi H.J., 2003. Hysteresis identification of polymethylaniline-based ER fluid using Preisach model. Mater. & Design 24, 53-61.

Helber R., Doncker F., Bung R., 1990. Vibration attenuation by passive stiffness switching mounts. J. Sound Vibrat. 138, 47-57.

Hoffman, R. L., 1972. Discontinuous and Dilatant Viscosity Behavior in Concentrated Suspensions. I. Observation of a Flow Instability. Transactions of the Society of Rheology 16(1), 155-174.

Hoffman, R.L., 1974. Discontinuous and dilatant viscosity behavior in concentrated suspensions. II. Theory and experimental tests. Journal of Colloid and Interface Science 46(3), 491-506.

Hoffman, R.L., 1982. Discontinuous and dilatant viscosity behavior in concentrated suspensions III. Necessary conditions for their occurrence in viscometric flows. Advances in Colloid and Interface Science 17(1), 161-184.

Hoffman, R.L., 1998. Explanations for the cause of shear thickening in concentrated colloidal suspensions. Journal of Rheology 42(1), 111-123.

Hunt, III., William C., Phelps, C.H. 1991. Method to reduce movement of a CPF device via a shear-thickening fluid. US4982792.

Jiang, W., Sun, Y., Xu, Y., Pen, C., *et al*, 2010. Shear-thickening behavior of polymethylmethacrylate particles suspensions in glycerine–water mixtures. Rheol Acta, 49(11), 1157-1163

Joanna, A., Elsa, R., Oleksander, S., Brijesh, V., 2007. Multi-layered apparatus for stopping projectiles. US20070178374A1.

Jolly, M.R., Bender, J.W., 2006. Field responsive shear thickening fluid. US20060231357.

Jones, D.A.R., Leary, B., Boger, D.V., 1991. The rheology of a concentrated colloidal suspension of hard spheres. Journal of Colloid and Interface Science 147(2), 479-495.

Kalman, D.P., 2010. Microstructure and rheology of concentrated suspensions of near hard-sphere colloids. Ph.D. thesis, University of Delaware, Delaware.

Kim J.H., Fang F.F., Choi H.J., Seo Y. 2008. Magnetic composites of conducting polyaniline/nano-sized magnetite and their magnetorheology. Mater Lett 62, 2897-2899.

Laskowski, J., Kitchener, J.A., 1969. The hydrophilic—hydrophobic transition on silica. Journal of Colloid and Interface Science 29(4), 670-679.

Laun H.M., Bung R., Schmidt F., 1991. Rheology of extremely shear thickening polymer dispersions. J. Rheol. 35, 999-1034.

Lee Y.S., Wetzel E.D., Wagner N.J., 2003. The ballistic impact characteristics of Kevlar woven fabrics impregnated with a colloidal shear thickening fluid. J. Mater. Sci. 38, 2825-2833.

Liu B., Shelley, M., Zhang J., 2010. Focused force transmission through an aqueous suspension of granules. Phys. Rev. Lett. 105, 188301.

Li X. *et al*., 2008. Preparation of body armour material of Kevlar fabric treated with colloidal silica nanocomposite.

Plast. Rubber Compos. 37, 223–226.

Maranzano, B.J., Wagner, N.J., 2001. The effects of interparticle interactions and particle size on reversible shear thickening: Hard-sphere colloidal dispersions. Journal of Rheology 45(5), 1205-1222.

Maranzano, B.J., Wagner, N.J., 2001. The effects of particle size on reversible shear thickening of concentrated colloidal dispersions. Journal of Chemical Physics 114(23), 10514-10527.

Melrose, J.R., Ball, R.C., 2004. Continuous shear thickening transitions in model concentrated colloids—The role of interparticle forces. Journal of Rheology 48(5), 937-960.

Mewis, N.J.Wagner, Norman, J, 2012. Colloidal Suspension Rheology. Cambridge University Press.

Montgomery T. Shaw, William J. MacKnight, 2005. Introduction to Polymer Viscoelasticity, 3rd Edition. Wiley-Interscience

Plant, D.J., 2010. Flexible energy absorbing material and methods of manufacture thereof. US20100086747.

Raghavan, S.R., Khan, S.A., 1997. Shear-Thickening Response of Fumed Silica Suspensions under Steady and Oscillatory Shear. Journal of Colloid and Interface Science 185(1), 57-67.

Roché, M., Kellay, H., Stone, H. A., 2011. Heterogeneity and the role of normal stresses during the extensional thinning of non-brownian shear-thickening fluids. Phys. Rev. Lett. 107, 134503.

Rosen B.A., Nam Laufer C.H., Kalman D.P., Wetzel E.D., Wagner N.J., 2007. Multi-Threat Performance of Kaolin-Based Shear Thickening Fluid (STF)-Treated Fabrics. Proceedings of SAMPE 2007. Baltimore, MD. June 3-7.

Sauer, B.B., Samant K.R. Trentacosta J.D., 2009. Fibrous structure useful in article e.g. body armour containing a combination of treated and untreated layers comprises a fibre and a high viscosity polymer that has specific glass transition temperature. US7556857.

Sauer, B.B., Samant, K.R. Trentacosta J.D., 2005. Ballistic Performance enhancement of fibre structure. US0282007.

Savins, J.G. 1968. Method of fracturing a subterranean formation with a shear thickening liquid. US3378073.

Savins, J.G., Metzner, A.B. 1968. Power transmission device employing a shear thickening liquid. US3400796.

Schuster, D.H.P., Fels, G.G.A., 1998. Material for antiballistic protective clothing. US5854143.

Seshimo, K. 1988.Viscoelastic damper. US4759428.

Shenoy S.S., Wagner N.J. and Bender J.W., 2003. E-FiRST:Electric field responsive shear thickening fluids. Rheol Acta 42, 287-294.

Smith, M. I., Besseling, R., Cates, M. E., Bertola, V., 2010. Dilatancy in the flow and fracture of stretched colloidal suspensions. Narure Commun.1, 114-115.

Ueno, K., Imaizumi, S., Hata, K., Watanabe, M., 2009. Colloidal Interaction in Ionic Liquids: Effects of Ionic Structures and Surface Chemistry on Rheology of Silica Colloidal Dispersions. Langmuir 25(2), 825-831.

Ueno. K, Watanabe, Masayoshi. 2011. From Colloidal Stability in Ionic Liquids to Advanced Soft Materials Using Unique Media. Langmuir 27(12),9105-9115

UK company, d3o, http://d3olab.com. (Accessed on: May 18, 2010).

Waitukaitis, S. R., Jaeger, H. M., 2012. Impact-activated solidification of dense suspensions via dynamic jamming fronts. Nature 487, 205-209.

Wagner, N., Kirkwood, J. E., Egres Jr, R.G., 2010. Shear thickening fluid containment in polymer composites. US20100071893A1.

Wagner, N.J., Brady, J.F., 2009. Shear thickening in colloidal dispersions. Physics Today 62(10), 27-32.

Wagner, N.J., Wetzel, E.D. 2009. Conformable ballistic resistant and protective composite materials composed of shear thickening fluids reinforced by short fibres. US20090004413.

Wagner, N.J., Wetzel, E.D., 2007. Advanced body armour utilizing shear thickening fluids. US7226878.

Wagner, N.J., Wetzel, E.D., 2009. Advanced body armour utilizing shear thickening fluids. US7498276.

Wagner, N.J., Wetzel, E.D., 2009. Conformable ballistic resistant and protective composite materials composed of shear thickening fluids reinforced by short fibres. US20090004413.

Wagner, N.J., Wetzel, E.D., Ronald G., Egres J.R. 2006. Shear thickening fluid containment in polymer composites. US0234572.

Wasserman, S.H.W., Cogen, J.M., Person, T.J., Gross, L. H., 2010.Cable comprising a shear thickening composition. US20100027948A1.

Wen, W.J., Huang, X.X., Yang, S.H., Lu, K.Q., Sheng, P., 2003.The giant electroheological effect in suspensions of nanoparticles. Nat Mater 2, 727-730.

Williams, T. H., Day, J., P, Simon, 2009. Surgical and Medical Garments and Materials Incorporating Shear Thickening Fluids. US2007000440086.

Zhang X., Li W., Gong X.L., 2008. Study on magnetorheological shear thickening fluid. Smart Mater. Struct. 17, 015051.